Agriculture
Canada

Research Branch
Direction générale de la recherche

Technical Bulletin 1991-5E

Technology of dormancy release in potato tubers

Canada

91--03913/

Technology of dormancy release in potato tubers

W.K. COLEMAN
Research Station
Fredericton, N.B.

G. HAWKINS
New Brunswick Department of Agriculture
Fredericton, N.B.

J. MCINERNEY and M. GODDARD
Department of Chemical Engineering
University of New Brunswick
Fredericton, N.B.

Technical Bulletin 1991-5E

Research Branch
Agriculture Canada
1991

Copies of this publication are available from
Director
Research Station
Research Branch, Agriculture Canada
P.O. Box 20280
Fredericton, New Brunswick
E3B 4Z7

Produced by Research Program Service

© Minister of Supply and Services Canada 1991
Cat. No. A54-8/1991-5E
ISBN 0-662-18550-1

Cover illustration
The dots on the map represent
Agriculture Canada research
establishments.

CONTENTS

ACKNOWLEDGMENTS iii

SUMMARY iv

INTRODUCTION 1

Tuber dormancy 1

Dormancy release by external agents 2

Objectives of current research 3

BROMOETHANE 4

Properties 4

Toxicology 5

Mutagenicity and carcinogenicity 7

Flammable hazard 7

EVALUATION OF DORMANCY RELEASE 8

Controlled environment evaluation 8

Field evaluation 16

Disease detection in treated tubers 16

EXPERIMENTAL ADSORPTION SYSTEMS 17

Screening of adsorbents 17

Adsorption of bromoethane 20

Regeneration of YAO adsorbent 29

Bench-scale experiments 30

CONCLUSIONS 37

Potential for environmental containment 37

Pilot plant design 38

REFERENCES 43

APPENDIX I: Theoretical Analysis 47

Theoretical Analysis 48

ACKNOWLEDGMENTS

This work was supported by the federal/provincial Industrial Innovation and Technology Development Subsidiary Agreement (grant no. 9963-121-109) between Canada and the province of New Brunswick.

SUMMARY

Potato tuber dormancy can hinder production of basic nuclear seed stock from greenhouse tubers, sales of Canadian seed potatoes to early export markets and rapid post-harvest disease testing. Tuber dormancy can be released immediately in a wide range of commercially important North American cultivars by brief treatment (1 - 2 days) with bromoethane vapor. The development of a complete, large scale technology for bromoethane application and its safe removal through a capturing techinque is necessary for successful application of this dormancy release method. Results of screening studies for adsorbents indicate that both YAO and HTO activated carbon have a similar high capacity for bromoethane. Both compounds have a low affinity for water adsorption, and adsorb and desorb bromoethane quickly and easily. The more economical YAO is the adsorbent suggested for a bromoethane adsorption system.

Based on the present study, a plausible design for a dormancy release facility is presented. This facility should allow the current objectives of the North American seed potato industry to be met in a safe and environmentally responsible manner.

RÉSUMÉ

La dormance peut avoir un effet négatif sur la production de matériel de semence de base à partir de tubercules de pommes de terre provenant de serres, sur les ventes hâtives de pommes de terre de semence canadiennes sur les marchés extérieurs et sur la rapidité du dépistage phytosanitaire àprès la récolte. Une exposition brève (1 - 2 jours) des tubercules de pommes de terre aux vapeurs de bromure d'éthyl peut rompre la dormance immédiatement chez plusieurs des variétés nord-américaines qui sont d'importance commerciale. L'application réussie de cette méthode pour rompre la dormance nécessite le développement à grande échelle de toute la technologie requise pour l'application du bromure d'éthyl et sa recapture. Les résultats de tests de sélection indiquent que les charbons activés YAO et HTO ont des niveaux d'adsorption du bromure d'éthyl qui sont similaires et élevés. Les deux produits ont peu d'affinité pour l'eau par adsorption mais font rapidement et facilement l'adsorption et la désorption du bromure d'éthyl. Par ce qu'il est plus économique que le HTO, la YAO est recommandé pour une système d'adsorption du bromure d'éthyl.

La structure de base d'une unité servant à rompre la dormance des tubercules en utilisant le bromure d'éthyl est présentée. Cette unité devrait permettre de satisfaire les objectifs de l'industrie de la pomme de terre nord-américaine de façon sécuritaire et tout en respectant l'environnement.

INTRODUCTION

The potato (*Solanum tuberosum* L.) tuber is currently among the top five food crops in the world in terms of production volume, dollar value of production, edible energy, and protein yield per hectare; it is grown in more countries than any other crop except maize (Horton and Sawyer 1985). Although tuber dormancy is a desirable trait for the food industry in terms of high-quality commodity storage, there are crucial times in the potato seed industry when tuber dormancy can hinder production and sales.

TUBER DORMANCY

The potato tuber is a modified stem structure or stolon, which usually develops below ground as a consequence of the swelling of the subapical portion of the stolon with the simultaneous accumulation of starch and proteins. A tuber is considered dormant if the buds of this organ are unable to grow at favorable temperatures.

Tuber dormancy proceeds in a cultivar-specific manner because of a hypothetical balance of endogenous plant growth inhibitors and promoters where dormancy release involves a shift in the ratio in favor of promoters and subsequent establishment of positive feedback between the bud and mobilized food reserves (Coleman 1987). The endogenous promoters are believed to include cytokinins, gibberellins, and possibly ethylene; at least some of the inhibitors are present in an "inhibitor β" complex of which abscisic acid may be a major active component.

DORMANCY RELEASE BY EXTERNAL AGENTS

Although numerous chemicals have been found to reduce the duration of tuber dormancy, commercial exploitation has been unsuccessful. Substances used to date have been quite wide ranging in chemistry and have varied from gasoline or ammonia vapors to water or carbon dioxide (Coleman 1987). Large-scale methods of dormancy release must be based on the following practical considerations: ease of application, effectiveness, cost, environmental concerns, safety, and health aspects. Using these criteria, the current use of Rindite vapor at room temperature (a mixture of seven parts by volume of ethylene chlorohydrin, three parts 1,2-dichloroethane and, one part carbon tetrachloride) is unsatisfactory. For example, ethylene chlorohydrin, the major component of Rindite, induces cumulative kidney and liver degeneration at concentrations of 1-20 ppm (Department of Health, Education and Welfare 1978; L.F. Juodeika 1981, personal communication). Although Rindite presents no direct flammable hazard, the presence of the Rindite components in a fire fueled by other materials would present a significant safety hazard through possible exposure to ethylene chlorohydrin vapor.

First described in 1945 (Denny 1945), commercial use of Rindite has been attempted with only limited success because of the highly toxic nature of its components. However, bromoethane appears to be a potentially suitable chemical. This substance was first described as an effective agent for dormancy release by McCallum in a brief annual report (McCallum 1909). Subsequent evaluations of bromoethane were carried out by researchers at the Boyce Thompson Institute (Denny 1926A, 1926B; Miller 1934). Miller's study suggested that bromoethane was ineffective as a dormancy-releasing agent for potato. However, Miller applied only 25% of the amount of bromoethane shown by McCallum to be necessary to break

dormancy. Consequently, this promising agent appeared to need additional evaluations in the context of current requirements of the North American seed potato industry.

Recent work indicates bromoethane (BE) vapor is a very suitable candidate because it is as effective as Rindite, easy to apply, inexpensive, and possesses low toxicity (Coleman 1983, 1984; Coleman and Coleman 1986; McDonald and Coleman 1988).

OBJECTIVES OF CURRENT RESEARCH

Dormancy of potato tubers affects the seed potato industry in three major ways:

(1) Many North American and European cultivars have been unable to penetrate the early tropical and subtropical export seed markets because of a cultivar-specific and "innate" dormancy period. In addition, Canadian seed exporters have experienced dormancy problems in some South American and Mediterranean rim countries with traditional North American cultivars.

(2) The production of basic nuclear seed stock from greenhouse tubers is rapidly becoming an integral part of seed-production programs. However, greenhouse tubers possess an intense dormancy that appears to be more difficult to release than normal field-grown material. A consistent dormancy breaking method to maximize efficiency and turnaround time is required.

(3) Timely postharvest test results are required by potato-seed tuber growers as an essential component of their marketing strategy. Currently, most rapid postharvest test procedures require observation of field-grown plants derived from tubers that have had their dormancy broken. Even if postharvest testing becomes greenhouse or laboratory based, there will be a requirement for a

procedure to break dormancy but not to interfere with the detection of disease.

At present, no existing technology in North America or Europe addresses the problem of potato tuber dormancy as a major limiting factor in the seed export industry. The present research addresses this problem in terms of fumigant selection, evaluation, and environmental containment.

BROMOETHANE

PROPERTIES

Bromoethane (ethyl bromide, monobromoethane, bromic ether, hydrobromic ether) is a very volatile, clear, and colorless liquid (Table 1). This substance is made commercially by refluxing ethanol with hydrobromic and sulfuric acids, and removing bromoethane by distillation (Blatt 1960). A second commercial method uses gamma irradiation from cobalt-60 of hydrogen bromide and ethylene followed by a caustic scrubber system to remove unreacted hydrogen bromide (Harmer and Beale 1963). This method was used by Dow Chemical in the 1960s to produce about 500 tonnes of bromoethane annually. The process is exothermic and requires the gamma radiation only to initiate the process. Minor contaminants of commercially prepared bromoethane can include bromide or sulfate salts, ethanol, water, ethyl ether (up to 0.7%), hydrobromic acid, or ethylene. Ethylene dibromide may be a trace contaminant in bromoethane at levels up to 0.01% (D.A. Rickard, 1990, personal communication). Tests should be carried out on commercial bromoethane samples to select the lot with the lowest level of contaminants.

Bromoethane is used as an ethylating agent in organic synthesis (Great Lakes Chemical Corp. 1981), although past uses included as a refrigerant, an inhalation anesthetic, and a gasoline additive. It has been used as an

experimental fumigant to control mites in farm-stored grain in the United Kingdom (Bowley and Bell 1981) and was shown to be an effective sterilant of catgut against highly resistant spore formers when used at 8% concentration in 96% ethanol for 24 h at 56°C (Harmsen and Ostertag 1950).

Table 1 Physical properties of bromoethane

Property	Characteristics	Reference
Appearance	clear colorless liquid	
Autoignition point	511°C	Great Lakes Chemical Corp. 1981
Boiling point	38.2°C	Mumford and Phillips 1950
Flash point	-23.0°C	Great Lakes Chemical Corp. 1981
Formula	C_2H_5Br	
Freezing point	-119.0°C	Great Lakes Chemical Corp. 1981
Molecular weight	108.98	Windholz 1976
Refractive index, n_D(25°C)	1.421	Great Lakes Chemical Corp. 1981
RTECS number	KH6475000	
Solubility in water (g/100 g at 20°C)	0.914	Windholz 1976
Specific gravity (25°C/4°C)	1.451	Great Lakes Chemical Corp. 1981
Surface tension (dynes/cm at 25°C)	23.45	Mumford and Phillips Corp. 1950
Vapor density (air = 1)	3.75	Great Lakes Chemical Corp. 1981
Vapor pressure (mm Hg at 25°C)	469.0	Great Lakes Chemical Corp. 1981
Viscosity (centipoises at 25°C)	0.379	Mumford and Phillips 1950

TOXICOLOGY

When bromoethane is compared with the components of Rindite on the basis of health and safety, the preference for bromoethane is apparent. However, bromoethane is not without its hazards, and precautions must be taken in handling and usage.

Bromoethane has been described as a respiratory irritant and a hepato- and renal toxin. At high concentrations, it causes narcosis, which probably accounts for its early use as a human anesthetic (NIOSH 1978). Applied to humans as a respiratory anesthetic at a concentration of approximately 100 000 ppm (10% by volume), bromoethane caused some fatalities either immediately from respiratory or cardiac arrest or in a delayed fashion from its effects on the liver, kidneys, and heart. Exposure of four guinea pigs for 30 minutes to 24 000 ppm (2.4% by volume) was fatal to three of them within 3 days as a result of pulmonary congestion, centrolobular necrosis of the liver, and diffuse nephritis (Tatkin and Lewis 1983; NIOSH 1978). Repeated and prolonged exposure of skin to bromoethane can lead to dermatitis.

Because the ether-like odor of bromoethane is detectable at concentrations above 200 ppm, the threshold limit value was set at 200 ppm (890 mg/m^3) to avoid narcosis and other toxic effects. Symptoms of overexposure to bromoethane include eye irritation, vertigo, dermatitis, or signs of liver and kidney damage (Oettingen 1978; Sax and Lewis 1988). Severe exposure may result in a generally confused state that will need to be differentiated from other causes such as hypoglycemia, hyperglycemia, cerebrovascular accident, transient ischemic episodes, head injury, postepileptic confusion, heat stroke, drug abuse, toxic encephalopathy, meningitis, or encephalitis. Treatment for overexposure to bromoethane involves removal from exposure, washing of skin areas, and irrigation of the eyes. People with a history of skin, liver, kidney, or chronic respiratory disease may be at an increased risk from exposure (Proctor and Hughes 1978).

MUTAGENICITY AND CARCINOGENICITY

Although the components of Rindite are mutagenic and carcinogenic, bromoethane was initially believed to be nonmutagenic (L.F. Juodeika, 1981, personal communication). However, a study by Barber et al. (1981) reevaluated the traditional Ames *Salmonella*/microsome screening test for the detection of chemical mutagens using a closed, inert incubation system for testing the mutagenicity of volatile compounds. They noted that bromoethane probably is a direct-acting, base-pair mutagen. Further work supported this conclusion (Barber and Donish 1982; Barber et al. 1983).

An initial study of possible bromoethane carcinogenicity found that multiple injections of bromoethane into mice resulted in no significant increase in the frequency of lung tumors (Poirier et al. 1975). Long-term animal testing of bromoethane for carcinogenic activity is currently taking place as part of the national toxicology program of the United States Public Health Service. Preliminary results indicate that exposure of rats and mice to 100-400 ppm bromoethane 6 h a day, 5 days per week, for 2 years, resulted in significant neoplastic lesions (Roycroft 1989; Roycroft et al. 1989). Although workers using this fumigant would not be exposed to similar conditions, a dormancy release facility that uses bromoethane should be closely monitored during and after operation, and workers should be protected from inhalation of, and exposure to, the fumigant.

FLAMMABLE HAZARD

Bromoethane can become explosively flammable when mixed with air over the concentration range of 6.75-11.25% by volume. The fumigation process requires bromoethane at 6.6% by volume and should not pose an unusual fire hazard although

explosion-proof electrical utilities should be used during construction. All conventional extinguishing media (e.g., foams, dry powder, and carbon dioxide) are suitable for fire fighting. The presence of bromoethane in fires fueled by other materials may generate hydrogen bromide or bromine vapors requiring appropriate respiratory protection.

EVALUATION OF DORMANCY RELEASE

CONTROLLED ENVIRONMENT EVALUATION

Initial experiments in 1981 involved small quantities (2-4 kg) of seed tubers from different potato cultivars. After treatment with bromoethane vapor at room temperature for 24 h in airtight containers, the tubers were aerated for 2 to 4 h and then planted directly in clay pots under greenhouse conditions (18-24°C) and 16 h days created with supplemental incandescent and fluorescent light. Emergence, growth, and number of sprouts were recorded at 1-2 week intervals and analysis of variance was carried out on emergence time, rate of shoot elongation, and number of shoots.

When applied to whole tubers, which had been removed directly from the field 2 weeks after top killing in early August, bromoethane effectively broke dormancy and promoted multiple sprouting at a concentration of 294 000 mg/m^3 (i.e., 0.2mL liquid BE added for each litre of container volume) provided the tubers possessed a mature, intact periderm or "skin." Emergence gains of 40-70% were observed in five cultivars when whole tubers were planted (Coleman 1983). If the tubers were cut immediately after bromoethane treatment and then planted, emergence gains of 50-75% were observed (Tables 2 and 3; Coleman 1983).

The rate of shoot elongation increased significantly ($P < 0.05$) by 2.8 mm/day and there was no difference in bromoethane's effect among the

cultivars (Tables 4 and 5; Coleman 1983). Because of a strong apical dominance, the mean number of shoots per seed piece remained low although bromoethane significantly increased this number (Table 6).

Subsequent large-scale application of bromoethane to 50-kg tuber samples of 14 cultivars confirmed the effectiveness of this fumigant to significantly promote tuber dormancy release, subsequent sprout growth rate, and number of emergent shoots per tuber relative to untreated control tubers (Coleman 1984).

Table 2 Effect of bromoethane on shoot emergence from tubers of five different cultivars

Cultivar	Post-treatment handling*	Number of days to 50% emergence		Emergence gain (%)**
		Control	BE treated	
Russet Burbank	whole	100	53	+47%
	cut	80	40	+50%
Red Pontiac	whole	71	40	+44%
	cut	65	24	+63%
Bintje	whole	58	35	+40%
	cut	45	23	+49%
Kennebec	whole	75	25	+67%
	cut	75	22	+71%
Caribe	whole	90	37	+59%
	cut	75	19	+75%

* After treatment with liquid BE at 0.2 mL/L of fumigation chamber volume, tubers were either planted whole in the greenhouse or cut into seed pieces and then planted .

** $$\text{Emergence gain} = \left[\frac{\text{Control-BE treated}}{\text{Control}}\right] \times 100\%.$$

Table 3 ANOVA table for shoot emergence

Source of variation	D.F.	M.S.	F value
Cultivars	4	422.45	43.55*
Cutting	1	672.8	69.36*
BE	1	8652.8	892.04*
Cutting x BE	1	3.2	0.33 NS
Cultivar x cutting	4	37.8	3.89 NS
Cultivar x BE	4	166.05	17.12*
Error	4	9.7	

* $P < 0.05$.

Table 4 Effect of bromoethane* on mean rate of shoot elongation and mean number of shoots from tubers of five different cultivars

Cultivar	Post-treatment handling	Mean rate of shoot elongation (mm/day)		Mean no. shoots per seed piece	
		Control	BE treated	Control	BE treated
Russet	whole	3.2	7.3	1.1	1.7
Burbank	cut	8.0	8.5	1.1	1.2
Red	whole	4.2	8.8	1.4	1.9
Pontiac	cut	4.8	5.9	1.0	1.1
Bintje	whole	8.5	16.0	1.1	2.9
	cut	13.0	16.7	1.0	1.9
Kennebec	whole	4.8	5.1	1.1	1.4
	cut	4.3	7.4	1.0	1.1
Caribe	whole	5.2	6.0	1.0	1.7
	cut	4.7	7.4	1.0	1.1

* 0.2 mL BE/L.

Table 5 ANOVA table for rate of shoot elongation

Source of variation	D.F.	M.S.	F value
Cultivars	4	46.86	17.27*
Cutting	1	6.73	2.48 N.S.
BE	1	40.33	14.86*
Cutting x BE	1	1.92	0.71 N.S.
Cultivar x cutting	4	2.84	1.05 N.S.
Cultivar x BE	4	2.60	0.96 N.S.
Error	4	2.71	

* $P < 0.05$.

N.S. = not significant.

Table 6 ANOVA table for number of shoots

Source of variation	D.F.	M.S.	F value
Cultivars	4	0.21	12.43*
Cutting	1	0.72	43.10*
BE	1	1.35	80.72*
Cutting x BE	1	0.34	20.18*
Cultivar x cutting	4	0.03	1.99 N.S.
Cultivar x BE	4	0.22	13.18*
Error	4	0.02	

* $P < 0.05$.

N.S. = not significant.

Table 7 Effects of chemical treatments on tuber sprouting in three potato cultivars under New Brunswick field conditions

Cultivar	Treatment[1]	Mean no. days to 50% emergence		Mean no. sprouts/tuber	
Kennebec	BE	68.1		1.0	
	BE/BE	61.1		1.1	
	BE/BE+ETOH	33.1		1.6	
Katahdin	BE	35.1		1.4	
	BE/BE	42.9		1.4	
	BE/BE+ETOH	61.7		1.0	
Russet Burbank	BE	41.3		1.1	
	BE/BE	25.4		2.3	
	BE/BE+ETOH	35.7		1.2	
		se	df	se	df
Standard error of differences between:					
Two cultivar means		0.908	21	0.0175	21
Two treatment means		0.831	21	0.0175	21
Two treatment means for one cultivar		1.485	7	0.0331	7
Two cultivar means for one treatment		1.439		0.0344	

[1] BE - bromoethane vapor (0.3 mL/L) for 24 h.

BE/BE - bromoethane vapor (0.3 mL/L) for 24 h, aeration for 24 h and second treatment with bromoethane (0.3 mL/L).

BE/BE+ETOH - bromoethane vapor (0.3 mL/L) for 24 h and second treatment with bromoethane (0.3 mL/L) and ethanol vapor (0.2 mL/L).

Table 8 Effects of chemical treatments on tuber yield responses in three potato cultivars

Cultivar	Treatment[1]	Mean no. tubers (x 10^5/ha)	Mean total tuber fresh weight (x 10^3 kg/ha)	Mean no. grade A tubers (x 10^3/ha)	Mean no. grade B tubers (x 10^3/ha)
Kennebec	BE	2.139	7.148	4.3	55.9
	BE/BE	2.320	14.845	38.7	77.0
	BE/BE+ETOH	2.457	24.024	91.2	75.7
Katahdin	BE	2.414	23.563	89.9	59.0
	BE/BE	2.264	20.925	70.2	45.6
	BE/BE+ETOH	2.380	13.094	27.5	84.4
Russet Burbank	BE	4.489	27.124	69.3	147.6
	BE/BE	5.139	42.101	137.7	176.5
	BE/BE+ETOH	3.701	31.066	89.9	117.9

Standard error of differences between:	se	df	se	df	se	df	se	df
Two cultivar means	79.2	21	760.7	21	49.4	21	81.0	21
Two treatment means	128.4	21	638.5	21	76.6	21	96.4	21
Two treatment means for one cultivar	336.0	7	1180.7	7	202.5	7	273.9	7
Two cultivar means for one treatment	385.3		1106.0		229.8		289.0	

[1] BE = bromoethane vapor (0.3 mL/L) for 24 h.

BE/BE = bromoethane vapor (0.3 mL/L) for 24 h, aeration for 24 h and second treatment with bromoethane (0.3 mL/L).

BE/BE+ETOH = bromoethane vapor (0.3 mL/L) for 24 h, aeration for 24 h and second treatment with bromoethane (0.3 mL/L) and ethanol vapor (0.2 mL/L)/

FIELD EVALUATION

Basic nuclear stock seed tubers from the cultivars Kennebec, Russet Burbank, and Katahdin were top pulled on 28 May 1985 and harvested from the greenhouse at Bon Accord Elite Seed Potato Farm in early June 1985. They were immediately treated for 24 h at 24°C as follows: (a) bromoethane vapor (0.3 mL liquid BE per litre volume of chamber); (b) bromoethane vapor for 24 h, aeration for 24 h, and then a second treatment with bromoethane vapor for 24 h; and (c) bromoethane vapor, aeration for 24 h, and then a second treatment with bromoethane vapor and ethanol vapor (liquid at 0.2 mL/L) for 24 h (Coleman and Coleman 1986).

All tubers were planted on 18 June 1985 at the Fredericton Research Station in a randomized split plot design where the three cultivars were the main factors and the three treatments were the subfactors. Tubers were harvested in late October and number and fresh weight of individual tubers were noted.

There was significant interaction ($P < 0.01$) between cultivar and treatment effects in terms of mean number of sprouts per tuber and time to 50% emergence although treated tubers began to emerge within 4 weeks (Table 7). Similar trends were evident in tuber number, total tuber yield, and the number of grade A and B seed tubers (Table 8). Two consecutive bromoethane treatments (treatment b) gave the best overall response when the mean results of the subfactors were compared.

DISEASE DETECTION IN TREATED TUBERS

To date (1990), there is no evidence that bromoethane will give a different disease response in the treated tubers or resulting plants compared to Rindite. However, this situation requires further evaluation. A previous paper (McDonald

and Coleman 1984), which indicated the Rindite-treated tubers increased ELISA values for potato virus Y (PVY) in comparison to bromoethane-treated material, has since been shown to be incorrect (McDonald and Coleman 1988). Both fumigants are equally effective in breaking dormancy and increasing the ELISA values for PVY. Preliminary results (unpublished) suggest that the detection of potato mosaic virus is not differentially affected relative to Rindite.

In evaluations of dormancy-releasing chemicals on subsequent tuber response to dry rot (*Fusarium sambucinum* f.6), development of seed tuber breakdown was not affected significantly by pretreatment with either Rindite or bromoethane (Coleman and Murphy, 1990).

EXPERIMENTAL ADSORPTION SYSTEMS

A capture system using adsorption would allow temporary storage of bromotethane in an adsorbent before being released for subsequent treatment of fresh tuber samples. The current study outlines initial experiments in the development of an environmentally appropriate procedure for handling bromoethane vapor.

SCREENING OF ADSORBENTS

The objective of the screening studies was to select an adsorbent that would have a high capacity for bromoethane and a low affinity for water adsorption, adsorb bromoethane quickly, and desorb bromoethane easily.

The apparatus employed in preliminary screening and detailed studies of adsorbents is shown schematically in Fig. 1. The apparatus consisted of two sections. The first facilitated generation of air or helium gas streams with controlled bromoethane and water vapor contents. The second section was

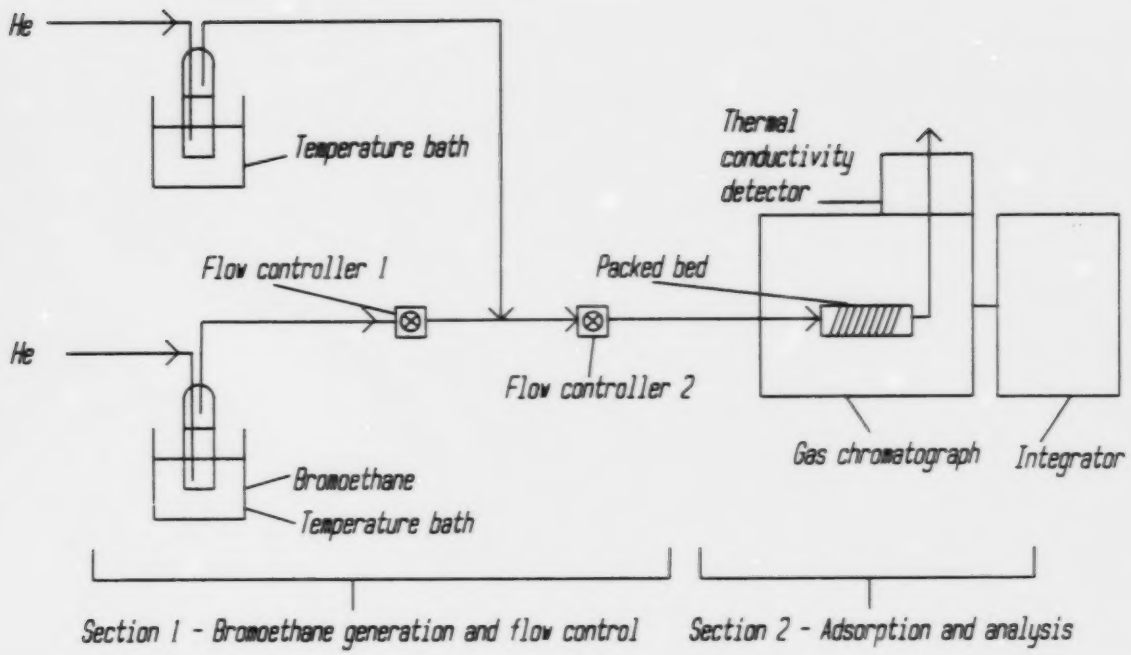

Fig. 1 A schematic diagram of the apparatus for the preliminary adsorption screening studies

comprised of a packed column containing the adsorbent under study and the gas detection system. Using air (or helium) as the carrier gas, the gas generation system functioned as follows.

Streams of compressed air were passed through gas wash bottles containing bromoethane and water, respectively. The temperature of the bottles was controlled by two Haake N3 constant temperature baths. The pressure of the inlet gas and the temperature fixed the bromoethane and water vapor concentration in the outlet streams. The rate of gas flow in the combined outlet streams from this section was controlled by two Matheson model 8200 mass flow controllers.

Gas entering the second section passed through a packed bed fabricated from 12.7 mm (1/2") O.D. copper tubing with 12.7 mm to 3.2 mm (1/8") Swagelok union fittings used as end caps. A Varian 3400 gas chromatograph equipped with a thermal conductivity detector was used to maintain the temperature of the packed column and measure gas concentrations in the outlet stream. The response of the detector was monitored with a Varian 4290 Integrator.

Four adsorbents were screened for adsorption of bromoethane from helium. They were:

- BOC - a carbon molecular sieve (British Oxygen)
- Amberlite AXD-4 - a polyethylene polymer (Rohme and Haas)
- HTO - a high-capacity activated carbon (Carbon and Filtration Canada).
- YAO - a medium - capacity activated carbon (Carbon and Filtration Canada).

The adsorbents were crushed and sieved to produce a 40-60 mesh material. Each adsorbent was tested in the "as received" condition and after regeneration with helium at 150°C. In the screening test, a concentration step chromatographic technique (Kumar 1978) was employed. A given weight of adsorbent was used to fill the packed bed (volume approximately 8 cc). The packed bed was

placed in the chromatograph oven, connected to the gas generation section, and then maintained at 33°C. The bromoethane generator was held at a pressure of 2.76×10^5 Pa (40 psia) and a temperature of 23°C to produce a stream of helium containing bromoethane at 22.1 mol%. In this set of experiments, water vapor was not added to the helium dilution stream. The mass flow controller on the outlet of the gas generation section was set to allow air to flow at 150 ml/min. The concentration of bromoethane in helium was increased in a step-wise fashion by varying the set-point on the other mass-flow controller, i.e., by decreasing the helium dilution factor. Because of bromoethane by the adsorbent, no immediate response to the step-change was detected with the chromatograph. The response of the detector was monitored until a complete breakthrough curve was achieved. The step increases in concentration were repeated until a bromoethane concentration of approximately 6.0 mol% was reached. The chromatographic response curves were analyzed to obtain retention times and equilibrium concentrations. The packed bed was weighed and the total amount of adsorbed bromoethane determined.

ADSORPTION OF BROMOETHANE

Pure component equilibrium adsorption isotherms over a wide range of concentrations extending to near saturation at a partial pressure of 0.062 atm were determined chromatographically for a number of possible adsorbents. A summary of the results of these experiments is presented in Table 9.

Table 9 Summary of adsorbent screening studies

Adsorbent	Type	Avg. Particle Size Tested (μm)	Avg. Pore Diameter (Å)	Typical Cost (1989$/kg)	Wt% Bromoethane adsorbed at 33°C and at 6.3 kPa BE
BOC	carbon	442	2.5	10	< 1
YAO	carbon	507	3.20	3.5	59.34
HTO	carbon	475	3.20	7.0	59.32
XAD4	polystyrene	580	40.60	15	17.40

The carbon-molecular sieve (BOC) was the first of the three carbon-based adsorbents studied. Only small molecules can be admitted into the structure of this sorbent because of the small size of the pores. Results of the adsorption equilibria indicated that less than 1 wt% was adsorbed at 33°C suggesting that bromoethane could not penetrate the pores of the adsorbent. Clearly, an adsorbent with a larger pore size would be required to achieve a higher bromoethane capacity.

Another adsorbent that showed a small capacity for bromoethane was a synthetic resin, XAD-4. At 33°C, the maximum capacity after regenerating the sample at 150°C was 17.4 wt% bromoethane. The high cost, coupled with the low capacity and a high affinity for water, would make this an unsuitable adsorbent for an adsorption system (Fig. 2).

Equilibrium isotherms for two activated carbon samples, YAO and HTO, were determined for samples both as they were received from the manufacturers and after regeneration at 150°C. Fig. 3 shows that for YAO, the capacity for bromoethane is higher throughout the range of partial pressures used in these

experiments. The difference in the adsorbed phase concentration may result from water present on the adsorbent when it is received. By regenerating the samples at 150°C, the water is removed and a higher capacity for bromoethane is achieved. Fig. 4 shows little difference in adsorption equilibrium for the high surface area HTO when compared with YAO, suggesting that either would be suitable adsorbents. Because HTO costs more, this sample was eliminated as a possible adsorbent, and further studies on the economically attractive YAO were conducted.

The adsorption of bromoethane on YAO was also determined at 50°C to estimate the heat of adsorption. In the limiting case, when the concentration of bromoethane approaches zero, the heat of adsorption is approximately 5.4 kcal/mol indicating that bromoethane is only weakly held by the adsorbent at low concentrations. The practical implications of this value for the heat of adsorption is that heating ($\leq$ 150°C) or mild heating with vacuum will remove the bromoethane from the adsorbent. Fig. 4 shows the adsorption equilibria determined at two temperatures.

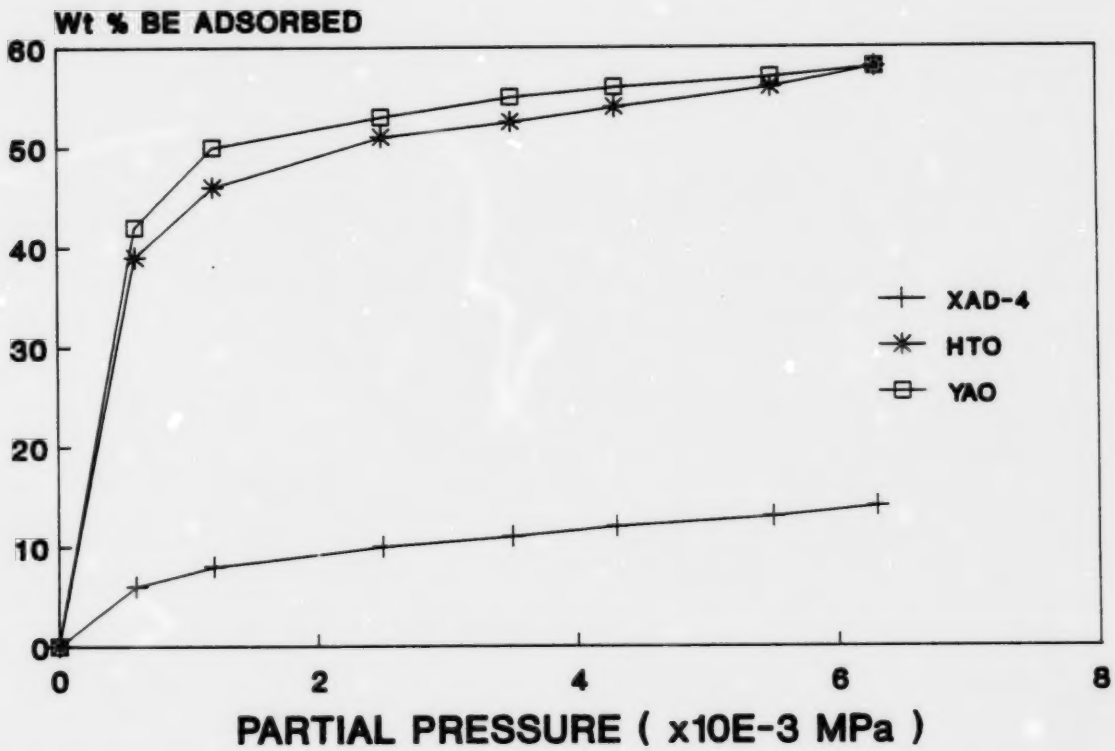

Fig. 2 Adsorption equilibria for bromoethane on YAO, HTO and XAD-4 adsorbents at 33℃

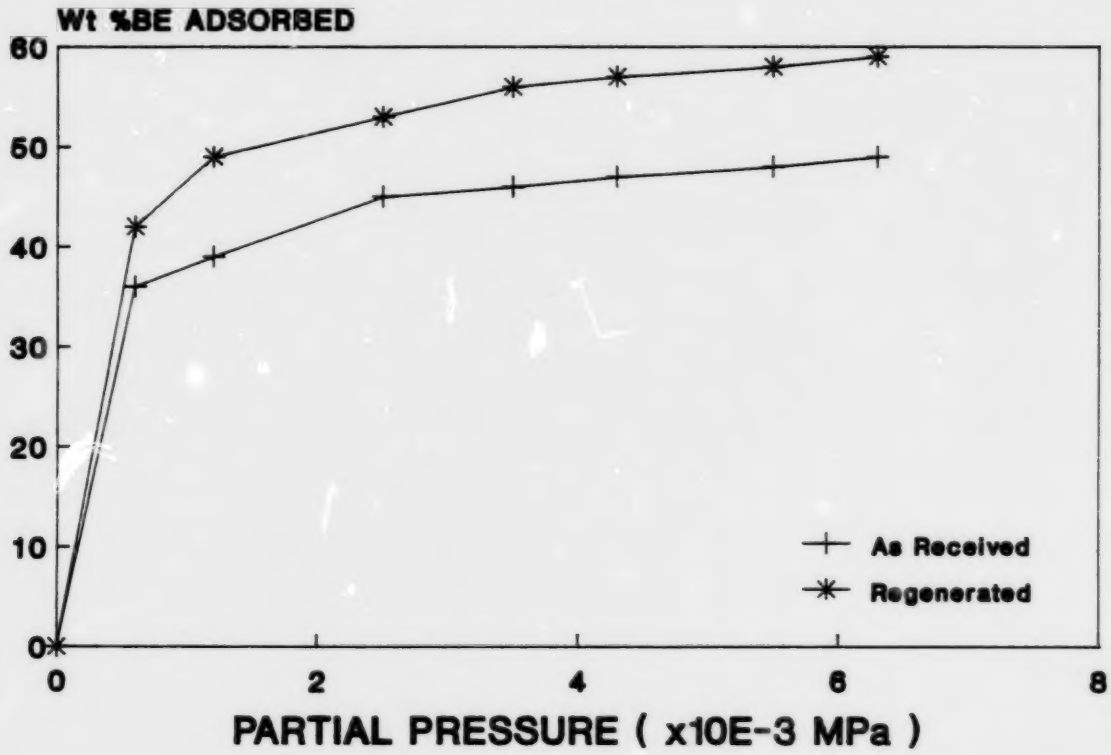

Fig. 3 Adsorption of bromoethane on the "as received" sample of YA0 and after regeneration at 150°C

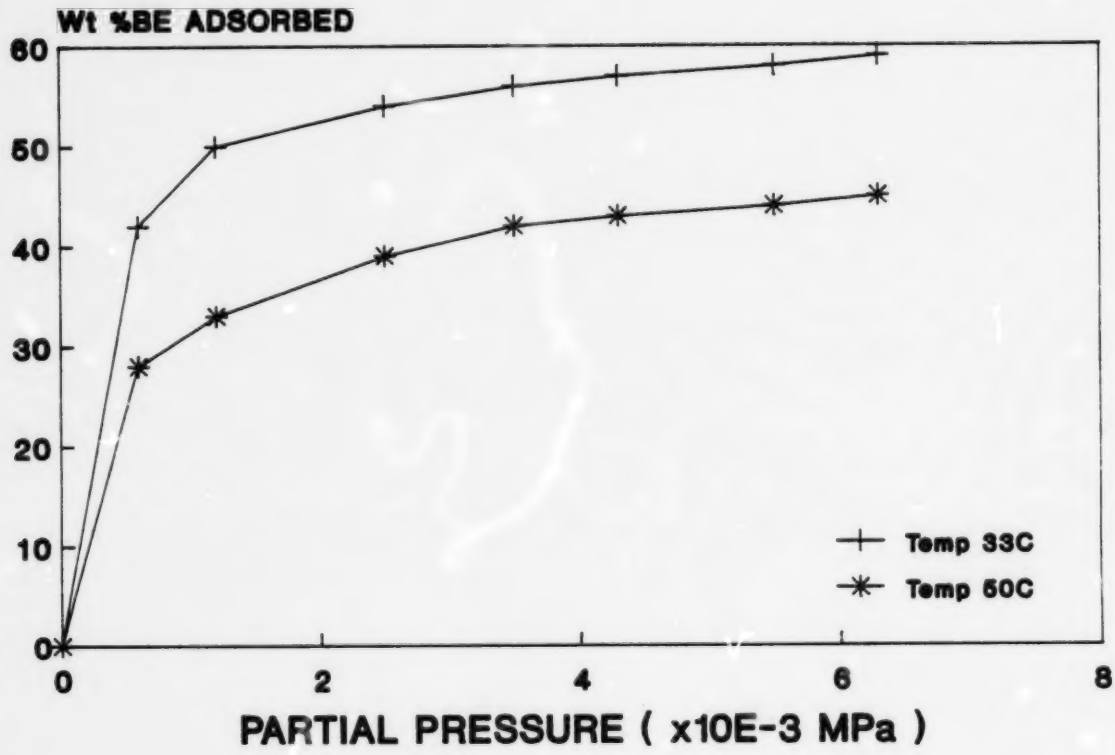

Fig. 4. A comparison of the adsorption equilibria for bromoethane on YA0 at 33°C and 50°C

For the pure component adsorption isotherms, helium was used as a nonadsorbing carrier gas. However, in a facility for exposing seed potatoes, bromoethane would be recovered from a mixture of air, bromoethane, water, and compounds released by the seed potatoes. A series of experiments were conducted to determine how the bromoethane concentration on YAO would be affected with air as a carrier gas and water present in the mixture.

Adsorption isotherms presented in Fig. 5 showed only a slight decrease in the adsorptive capacity for bromoethane when air, compared with helium, is used as a carrier gas. The introduction of water in the mixture reduced the capacity from 57 to 56 wt% for bromoethane.

Shown in Fig. 6 are breakthrough curves of bromoethane as a function of time using helium and air as carrier gases, as well as an experiment in which water vapor was present at 40-50% relative humidity. The breakthrough curve for the experiment using the helium carrier is delayed compared with the curves for air and air + water. In the air and air-water experiments, bromoethane has insufficient time to adsorb onto the surface of the activated carbon and will easily pass through the adsorption column (i.e., it has an early breakthrough). For the experiments using helium, bromoethane adsorption occurs quickly and so the breakthrough is delayed. Note that although the detector response for the air and air-water breakthrough curves are not normalized (the attenuation settings were different for each experiment), the curves indicate similar early breakthrough of bromoethane.

To summarize, these data suggest that even at high concentrations of water, YAO-activated carbon does not have a strong affinity for water, and the capacity for bromoethane is maintained at the values measured in the absence of water. Analysis of the breakthrough curves indicates that a longer period (i.e., a

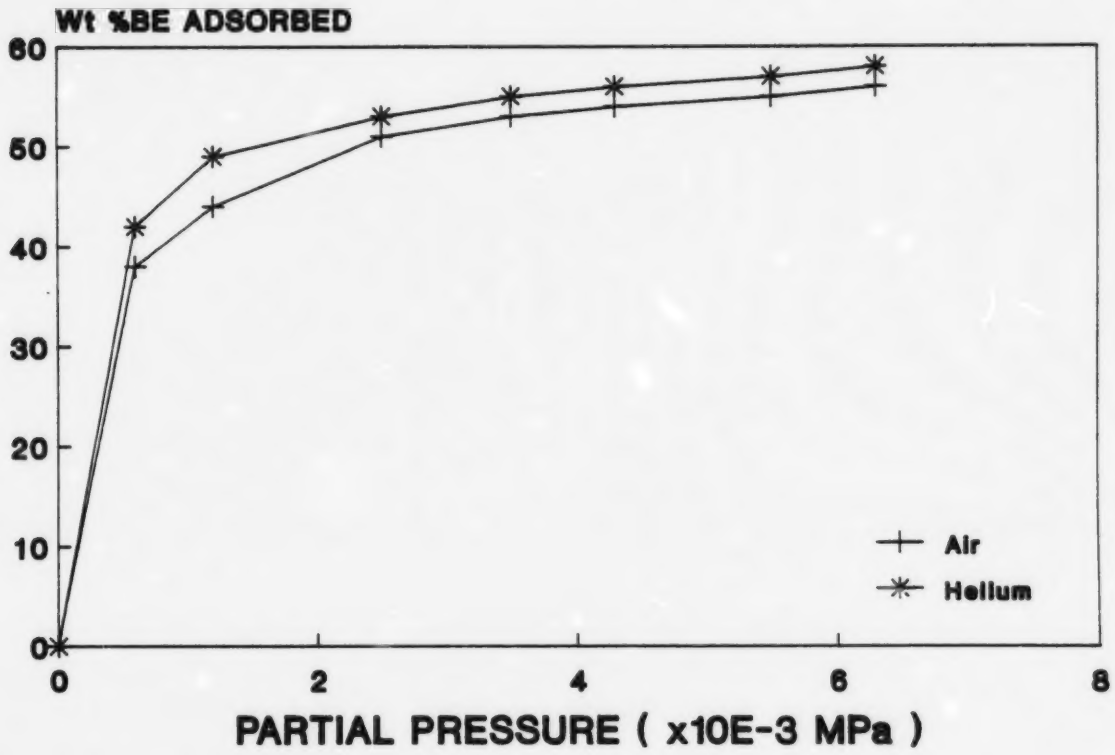

Fig. 5. A comparison of the adsorption equilibria for bromoethane from a mixture of BE-helium and BE-air on YA0 at 33℃

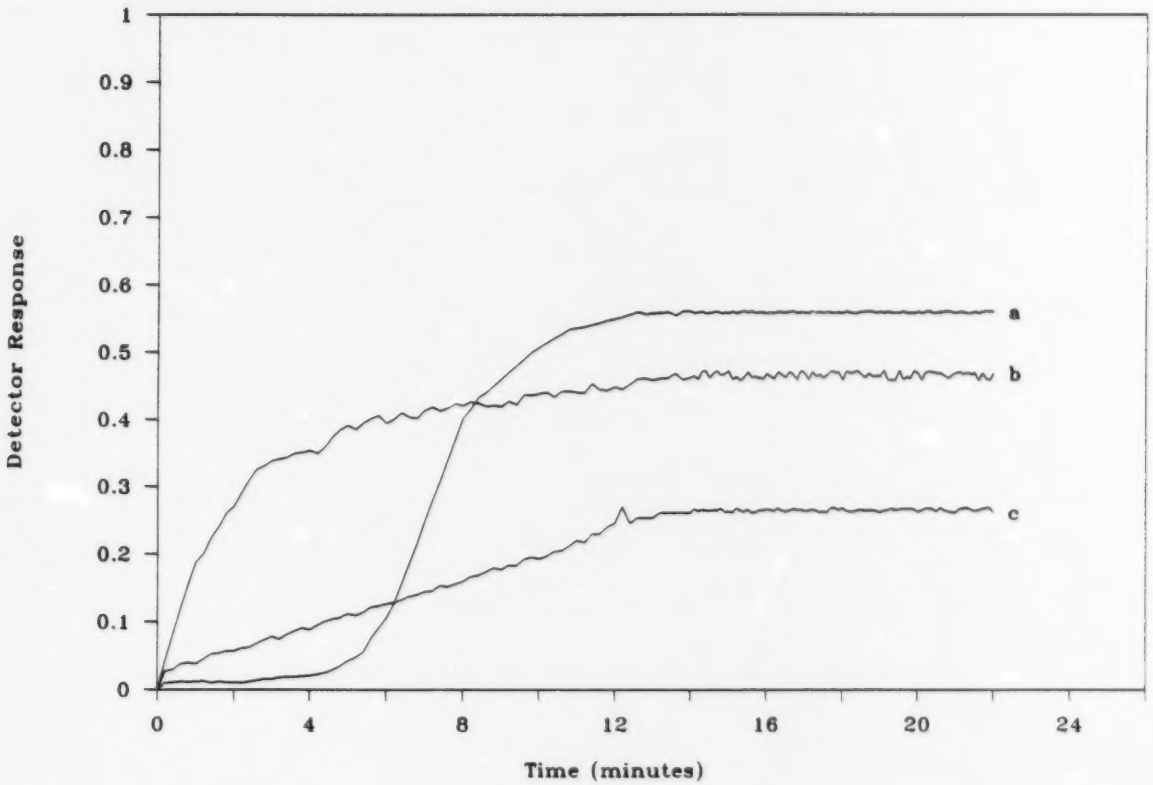

Fig. 6 Breakthrough curves of bromoethane from three mixtures of bromoethane - helium (a), bromoethane - air - water (b) and bromoethane - air (c)

longer residence time) is required for equilibrium to be achieved when bromoethane is adsorbed from air, or from a mixture with water vapor.

REGENERATION OF YAO ADSORBENT

Several techniques were used to regenerate YAO adsorbent, including:

(i) regeneration by air purge at 33°C or 150°C

(ii) regeneration by vacuum alone

(iii) regeneration by vacuum plus heating

The results with these methods are summarized in Table 10. As expected, the air purge and heat (150°C) treatment is the fastest method of regeneration. Unfortunately, this technique is not possible for a treatment facility, because only air from the chamber at room temperature is available to blow over the bed.

Vacuum desorption was effective at room temperature but only for the finer particle size (40 x 60) mesh. For the 4 x 8 mesh material, it appears that diffusion processes make desorption by vacuum effective only when the adsorbent bed is at temperatures greater than 100°C.

Table 10 Summary of regeneration technique for YAO - activated carbon

Method	Particle size (mesh)	Duration (hrs)	Wt% bromoethane initial	Wt% bromoethane final	Pressure (μm Hg)	Temp. (°C)
Air purge	40x60	16	57.3	11.3	760 K	33
Air purge and heat	40x60	4	57.3	0.0	760 K	33
Vacuum	40x60	4.5	57.3	3.6	31	23
Vacuum	4x8	12	15.0	13.4	60	23
Vacuum and heat	4x8	12	27.5	0.0	140	> 100

BENCH-SCALE EXPERIMENTS

The objective of this set of experiments was twofold: firstly, to determine the concentration of bromoethane in the exposure chamber after the gas had been circulated through a bed of YAO-activated carbon and equilibrium had been achieved. In this way a check of the results of the screening experiments could be made using an independent experimental method. Secondly, by monitoring the chamber contents as a function of time, the kinetics of adsorption could also be measured.

A schematic diagram of the bench-scale apparatus is presented in Fig. 7. The apparatus consisted of an airtight chamber to which bromoethane could be added and subsequently removed in adsorption. An attached blower recycled the air in the chamber through the adsorbent bed. Characteristics of the bench-scale adsorption setup are give in Table 11.

Table 11 Characteristics of the bench-scale adsorption apparatus

Chamber Volume	295 litres
Blower Flowrate	164 L/min (5.79 cfm)
Adsorbent	YAO - activated carbon
Size	4 x 8 MESH
Quantity	260 g
Bed Diameter	135 mm
Bed Depth	32 mm
Face Velocity	1.44 m/s

Initial bromoethane concentrations in a range of two to six mole percent were prepared in the exposure chamber by vaporizing a measured quantity of liquid bromoethane on a pre-heated surface. After complete vaporization an initial gas sample of 0.25 mL was taken with a gas-tight syringe. The blower motor was started causing the vapor in the chamber to circulate through the packed bed of YAO-activated carbon. Analysis of a gas sample for bromoethane, water and air with the chromatograph required approximately six minutes. This allowed sampling of gas in the chamber at only six to eight minutes intervals. Sampling was continued until equilibrium was achieved between the adsorbent bed and the air in the chamber. At the end of the test, the adsorbent was removed and weighed in order to determine the uptake of bromoethane. With 260 g of 4 x 8 mesh YAO-activated carbon a possible maximum uptake of 45 wt% could be achieved. Used adsorbent was regenerated by vacuum plus heating at 150°C.

Table 12 is a summary of experimental results designed to evaluate the concentration of bromoethane in an exposure chamber after the vapor had been circulated through a bed of YAO-activated carbon. Included in this table is the initial concentration of bromoethane in the chamber and the concentration after adsorption, the adsorbed phase concentration and the time to reach equilibrium

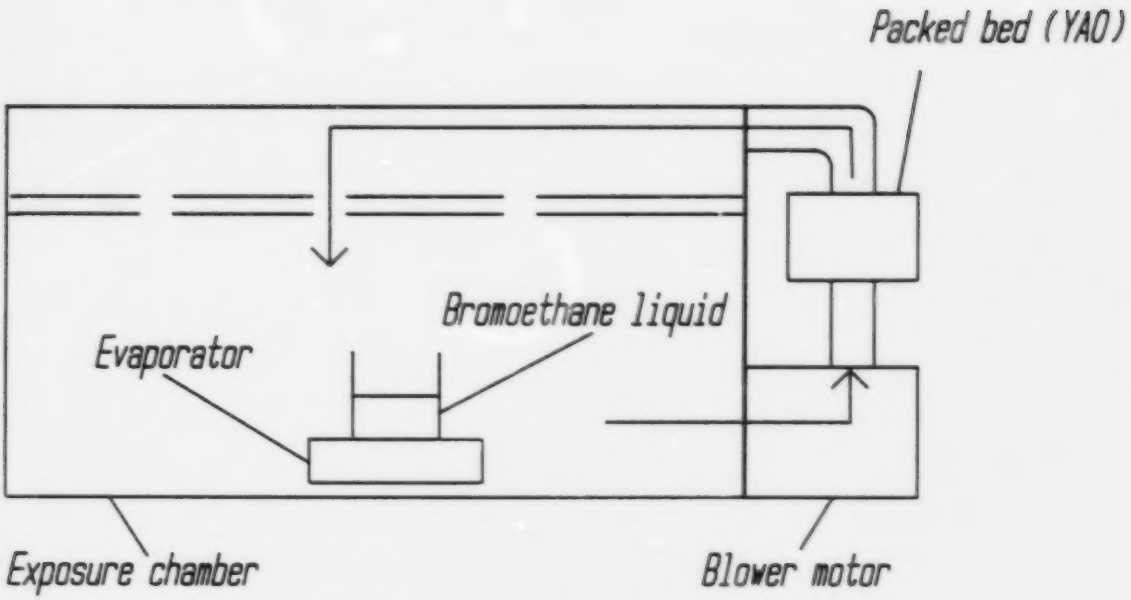

Fig. 7 A schematic representation of the apparatus used for the bench-scale adsorption experiments

at the experimental temperature. Plotted in Fig. 9 is the concentration of bromoethane in the chamber (mol%) as a function of time.

Fig. 8 shows the good agreement of the equilibrium isotherms obtained using the small bench-scale apparatus at 23°C and the isotherm obtained from the screening experiment at 33°C. The small difference between the two isotherms at the point they overlap may be accounted for by the difference in temperatures.

Mixtures of bromoethane in air and in air with water at 90% relative humidity were prepared for experiments 3 and 6. The results show that the adsorbed phase concentration of bromoethane is reduced slightly from 21.9 to 20 wt% by the presence of water and is similar to the results obtained in the screening studies.

Analysis of the kinetic results indicates that the rate of adsorption is reduced by the presence of water. In experiment 6, the equilibrium concentration in the chamber was achieved in 27 min. and in experiment 3, 16 min. was required for the bromoethane concentration in air to achieve equilibrium.

The practical implications of these results suggest that, although the adsorbed phase equilibrium may only be reduced slightly by a high concentration of water, the slow rate of adsorption must be allowed for and a longer residence time in the adsorption bed is required.

Table 12 Summary of small scale adsorption tests

Ept.	Bromoethane injected	Bromoethane conc. in air		Bromoethane adsorbed		Equilibrium reached **	Temp.
	(g)	initial (mol%)	equil. (mol%)	initial (wt%)	equil. (wt%)	(min)	(°C)
1	26.78	2.220	<0.001	0.0	9.9	15	23
2	57.50	5.320	0.158	9.9	30.1	20	23
3	57.06	4.014	0.055	0.0	21.9	16	23
4	39.97	2.780	0.018	0.0	15.0	12	23
5	82.85	5.750*	0.556	15.0	42.7	20	23
6	55.70	3.890*	0.081	00.0	20.0	27	27***

* Estimated initial concentration.
** Time at which first minimum bromoethane concentration reading reached.
*** Water vapor presence at 90% relative humidity.

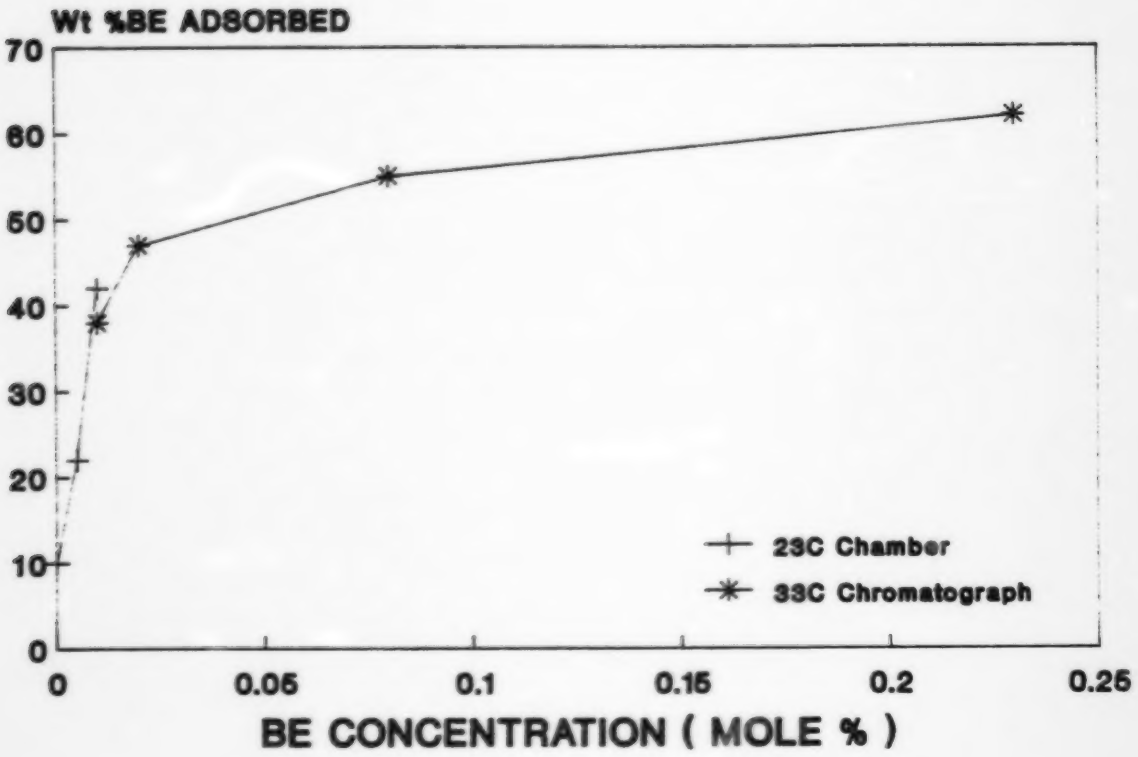

Fig. 8 Adsorption equilibria isotherms for bromoethane on YA0 at 23°C determined using the small bench-scale apparatus and at 33°C determined using the screening studies apparatus

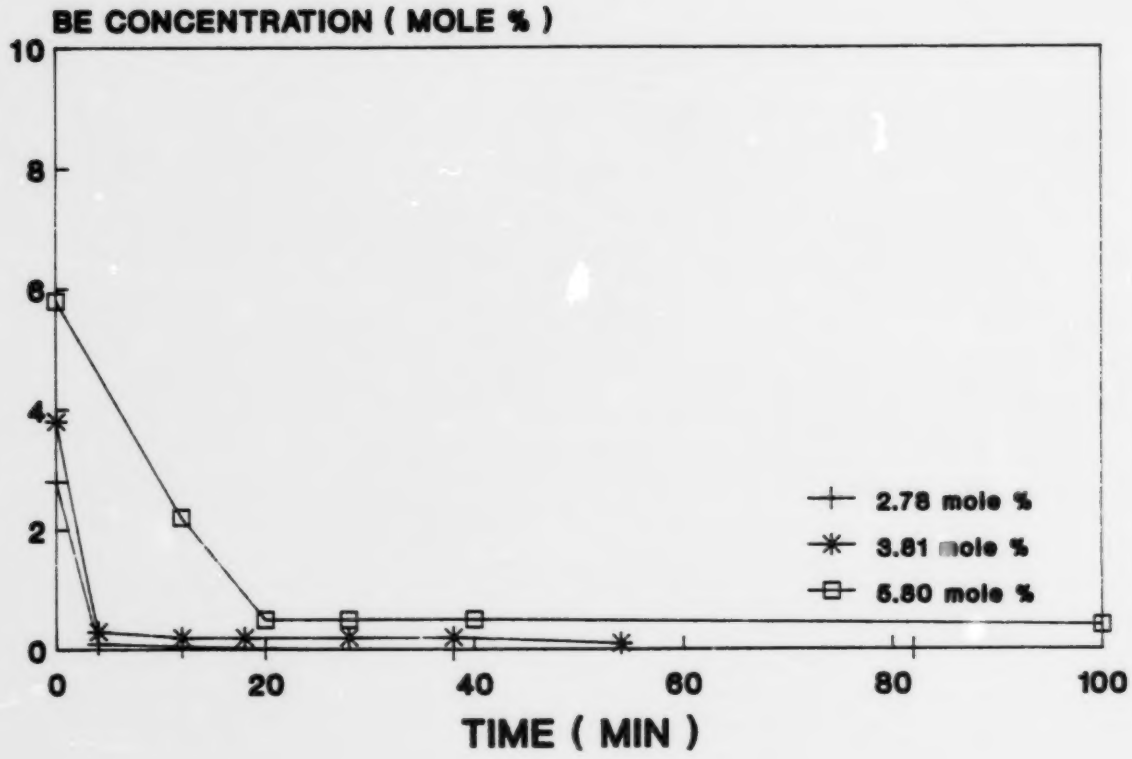

Fig. 9 Bromoethane concentration in the chamber of the bench-scale apparatus as a function of time for different initial concentrations of bromoethane in air

CONCLUSIONS

POTENTIAL FOR ENVIRONMENTAL CONTAINMENT

The development of a complete, large-scale technology for bromoethane application and its safe removal through a capturing technology is necessary for the successful application of a dormancy release technology.

The present study indicates that dormancy in seed potato tubers can be released immediately in a wide range of commercially important North American cultivars by treatment with bromoethane vapor. Based on the present study, a plausible design for a dormancy release facility can be presented (see "Pilot plant design" section below). This facility should allow the current objectives of the North American seed potato industry to be met in a safe and environmentally responsible manner.

Because treated tubers will not be used for human consumption, any residues (e.g., bromide) within the tubers should not be a problem.

Bromoethane appears to be as effective as Rindite in breaking tuber dormancy. However, bromoethane is superior in terms of method of application, environmental concerns, safety and health aspects, and cost. Although there is no evidence that bromoethane will give a different disease response in the treated tubers or plants compared with Rindite, further evaluations should be carried out (see "Disease detection in treated tubers").

The adsorption system is an appropriate technology for handling bromoethane in a treatment facility designed to break the dormancy period of seed potatoes. Results of the screening studies for adsorbents indicate that both YAO - and HTO - activated carbon have a high capacity for bromoethane that is essentially the same. The more economical YAO is the adsorbent suggested for a bromoethane adsorption system.

The release of water vapor from the tubers should saturate the surrounding air in the treatment facility during the dormancy release treatment, which may last 2-3 days at room temperature. Present results suggest that water vapor in a mixture of bromoethane and air only reduces the equilibrium concentration of adsorbed bromoethane slightly. However, the rate at which bromoethane equilibrium is achieved will be reduced by the presence of air and water. In view of the superior results with helium, the replacement of air with an inert gas such as nitrogen (an acceptable low cost alternative to helium) would improve the equilibrium rate and reduce the flammable hazard associated with bromoethane. No detrimental effects on dormancy release would be expected although a small scale experiment to test this supposition would be necessary.

The low heat of adsorption (5.4 kcal/mol) indicates that heating or mild heating coupled with vacuum will desorb bromoethane from the activated carbon. Because the effects of compounds released from the tubers on the adsorption capacity are not well understand or the flow rate of bromoethane has not been determined to achieve an efficient use of the adsorption process, a pilot plant is recommended.

PILOT PLANT DESIGN

The pilot plant is envisaged as two fixed beds of activated carbon with regeneration by vacuum and heating. Both beds in the system will be of equal size with an overdesign allowance of 25% for bromoethane capacity. All functions of the adsorption-recovery system will be monitored and regulated by a computerized control system. A schematic diagram is presented Fig. 10.

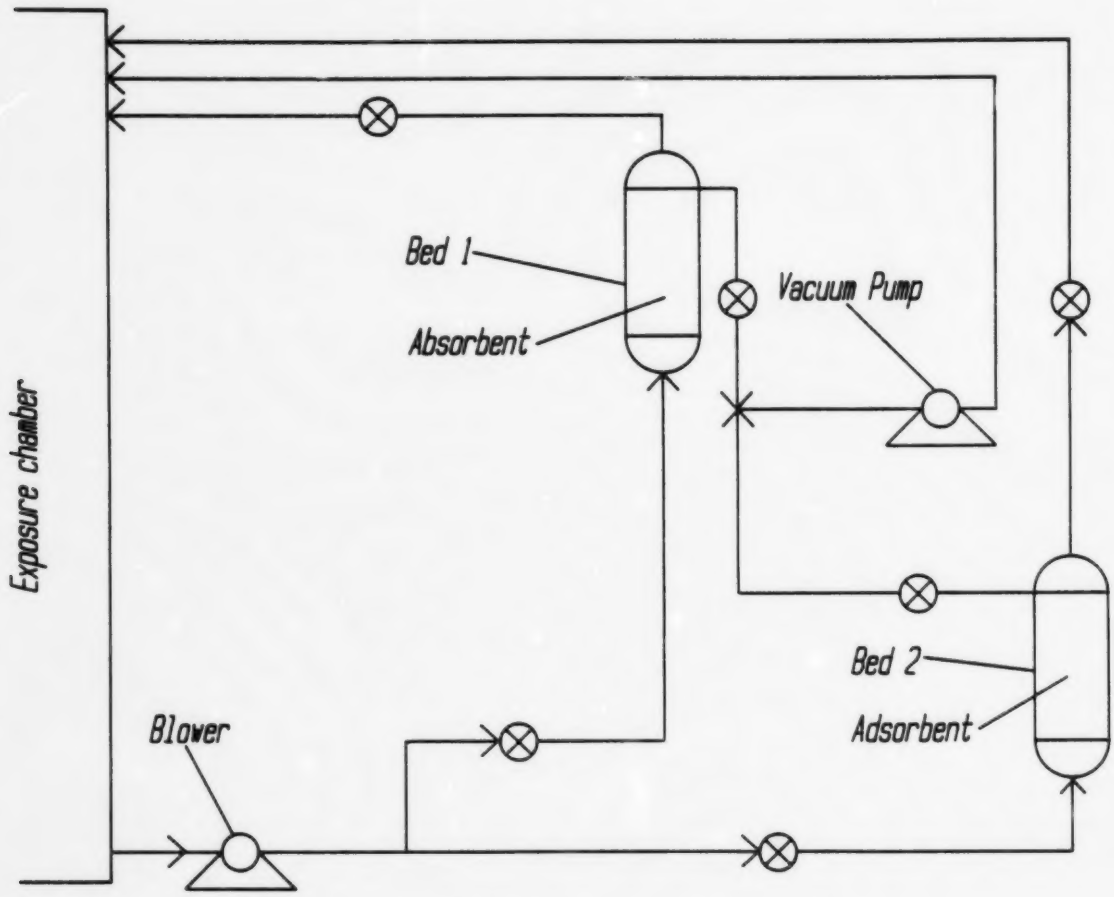

Fig. 10 A schematic diagram of an adsorption pilot plant for handling bromoethane

In this design, bromoethane is introduced to the exposure chamber via an automated dispensing and evaporation system. The tubers in the chamber are then exposed for the required time in two stages.

In the first stage of the bromoethane adsorption cycle, air from the chamber is blown through bed #1 until the concentration of bromoethane in the chamber reaches equilibrium, i.e., about 85% of the bromoethane is recovered. At this point, bed #1 is isolated and bed #2 is opened to the system. Air is circulated through bed #2 until the bromoethane concentration in chamber falls below the 200 ppm threshold level. Then bed #2 is isolated from the chamber.

The treated tubers are removed and the chamber is reloaded. Release of the bromoethane to the chamber is accomplished by heating of the bed to 150°C and imposing a vacuum. Any additional bromoethane required because of leakage or adsorption by the tubers is added by the automated dispensing system. Spent activated carbon after a number of adsorption cycles may be transferred pneumatically (using the blower) to containers for disposal.

A summary of the costs of materials for a pilot plant system is presented in Table 13 and the basis for this calculation is found in Table 14. It should be noted that quoted costs do not include delivery charges, installation and labor and technical assessment costs.

In the context of the proposed fumigation facility, future R & D areas that should be addressed include the following: (i) determining the appropriate concentration-time product to optimize the bromoethane treatment of seed tubers; (ii) determining the amount and type of residues associated with tubers and their containers; and, (iii) developing an acceptable treatment and post-treatment protocol for safely handling the seed potatoes.

Table 13 Materials and estimated costs for demonstration-scale pilot plant

Item	Detail	Quantity	Unit cost (1989$)	Price (1989$)
Adsorbent system	Stainless steel, 0.915 m (3 ft) dia. x 1.22 m (4 ft) chamber stands 250 mm SS vac.	2		
	valves, 40 SS vac. valves	4		
	67.9 m^3/h (40 cfm) vac. pump	1		
	heaters, thermocouples controller vac. sensors and display system controller	1		100 000
Activated carbon	YAO 6 x 16 mesh	350 kg	3.50	1 225
Blower	2038 m^3/h (1200 cfm), FRP	1	5 600	5 600
Compressor	for pneumatics	1	1 000	1 000
Piping	to adsorber beds, circulation	1	9 000	9 000
Circulating fans	for air mixing in chamber	2	1 500	3 000
Air filter system	for adsorption system	1	5 000	5 000
Control system	computer + relays			15 000
Bromoethane dispenser	pump, control valve, tank, evap.	1	4 500	4 500
Bromoethane detector	B & K model 1302 08 to 80 000 ppm	1	34 700	34 700
			component total	$179 025

Note: Because of time restrictions that may be placed upon construction and commissioning of the plant, the major components, i.e., adsorbent, beds, valves, and vacuum system, are priced as a manufactured unit. Because the high capacity of activated carbon for most organic compounds and the flexibility of the vacuum-heat regeneration regime, the facility should be able to handle other agricultural fumigants.

Table 14 Basis for pilot plant calculations

BASIS BROMOETHANE: 55.2 kg

BROMOETHANE @ 4 mol% (34 L of BE/L of chamber)

CHAMBER VOLUME: 284 m^3 (10 017 ft^3)

Bed #1 For adsorber bed assume 40 wt% adsorbed on bed #1 and equilibrium BE concentration of 0.60 @ 23°C bed designed with 25% additional capacity.

bulk density of adsorbent	440 kg/m^3	
weight of adsorbent in #1	172 kg	
volume adsorbent	0.391 m^3	(13.8 ft^3)
bed diameter	0.76 m	(2.5 ft)
bed length	0.85 m	(2.8 ft)
face velocity	0.51 m/s	(100 fpm)
blower capacity	0.47 m^3/s	(1000 cfm)
air changes/hour (chamber)	5.99	

Vacuum system:

target vacuum	50 μm Hg
volume BE adsorbed	11 344 L
capacity	850 L/min
pump down time to target vacuum	2.67 h

Bed #2 Bed size is the same as #1, which is probably cost effective if vessels are custom built. The second bed must have enough capacity to remove remaining bromoethane from chamber after bed #1 reaches equilibrium and is switched out of the recirculating mode. The remaining bromoethane in the chamber when bed #2 is switched in should be < 10 wt% of the adsorbent in bed #2. Based on laboratory-scale test the remaining bromoethane should be < 15% of the original, which would be 8.28 kg making a minimum bed size of 82 kg. A reasonable safety margin is thus maintained by making bed #1 and #2 of equal size.

REFERENCES

Barber, E.D.; Donish, W.H., 1982. An exposure system for quantitative measurements of the microbial mutagenicity of volatile liquids. Tice, R.R., Costa, D.L., Shaich, K.M.,eds., In Genotoxic effects of airborne agents, Plenum Press, New York.

Barber, E.D.; Donish, W.H., Mueller, K.R., 1981. A procedure for the quantitative measurement of the mutagenicity of volatile liquids in the Ames *Salmonella*/microsome assay. Mutat. Res. 90:31 - 48.

Barber, E.D.; Donish, W.H., Mueller, K.R., 1983. The relationship between growth and reversion in the Ames *Salmonella* plate incorporation assay. Mutat. Res. 113:89 - 101.

Blatt, A.H. ed., 1960. Organic syntheses. Collective volume I. 2nd. ed., John Wiley and Sons, Inc., New York.

Bowley, C.R.; Bell, C.H., 1981. The toxicity of twelve fumigants to three species of mites infesting grain. J. Stored Prod. Res. 17:83 - 87.

Coleman, W.K., 1983. An evaluation of bromoethane for breaking tuber dormancy in *Solanum tuberosum* L. Am. Potato J. 60:161 - 167.

Coleman, W.K., 1984. Large scale application of bromoethane for breaking potato tuber dormancy. Am. Potato J. 61:587 - 589.

Coleman, W.K., 1987. Dormancy release in potato tubers: A review. Am. Potato J. 64:57 - 68.

Coleman, W.K.; Coleman, S.E., 1986. The effects of bromoethane and ethanol on potato *(Solanum tuberosum)* tuber sprouting and subsequent yield responses. Am. Potato J. 63:373 - 377.

Coleman, W.K.; Murphy, A., 1990. Effect of dormany releasing chemicals on subsequent tuber response to *Fusarium sambucinum*. Am. Potato J. 67:133 - 136.

Denny, F.E., 1926A. Hastening the sprouting of dormant potato tubers. Am. J. Bot. 13:118 - 125.

Denny, F.E., 1926B. Second report on the use of chemicals for hastening the sprouting of dormant potato tubers. Am. J. Bot. 13:386 - 396.

Denny, F.E., 1945. Synergistic effects of three chemicals in the treatment of dormant potato tubers. Contribution Boyce Thompson Inst. 14:1 - 20.

Department of Health, Education and Welfare. 1978. Ethylene oxide, ethylene chlorohydrin and ethylene glycol. Federal Register 43:27474 - 27483.

Great Lakes Chemical Corp. 1981. Ethyl bromide: Material safety data sheet. 2 pp.

Harmer, D.E.; Beale, J.S., 1963. Radiation catalysis of ethyl bromide six months "on stream". Nucleonics 21:76 - 77.

Harmsen, H.; Ostertag, H., 1950. [The sterilizing effect of primary alcoholic salts of halogens. -Ger.]. Zentralbl. Bakteriol. 1 Abt. Orig. A 156(2):144 - 165.

Horton, D.; Sawyer, R.L., 1985. The potato as a world food crop, with special reference to developing areas. pp. 1 - 34, Li, P.H., ed., Potato physiology. Academic Press, New York.

Kumar, R., 1978. Binary mixtures of gases on zeolites: A study of sorption and kinetic behaviour by chromatography. Ph.D. thesis, University of New Brunswick, Fredericton, N.B.

McCallum, W.B., 1909. Twentieth Annual Report Univ. Arizona Exp. Stn. pp. 584 - 586.

McDonald, J.G.; Coleman, W.K., 1984. Detection of potato viruses Y and S in tubers by ELISA after breaking of dormancy with bromoethane or Rindite. Am. Potato J. 61:619 - 622.

McDonald, J.G.; Coleman, W.K., 1988. A re-evaluation of bromoethane in comparison to Rindite for the post-harvest detection of potato virus Y in tubers by ELISA. Am. Potato J. 65:547 - 550.

Miller, L.P., 1934. The effect of the alkyl halides on the respiration of potato tubers. Contribution Boyce Thompson Inst. 6:279 - 296.

Mumford, S.A., Phillips, J.W.C., 1950. The physical properties of some aliphatic compounds. J. Chem. Soc. 75:75 - 84.

NIOSH. 1978. Occupatio[illegible]l health guideline for ethyl bromide. U.S. Department of Health and Human Services. 4 pp.

Oettingen, W.F. von, 1978. The halogenated aliphatic, olefinic, cyclic, aromatic, and aliphatic-aromatic hydrocarbons including the halogenated insecticides, their toxicity and potential dangers. Public Health Service, U.S. Department of Health, Education and Welfare.

Poirier, L.A.; Stoner, G.D.; Shimkin, M.B., 1975. Bioassay of alkyl halides and nucleotide base analogs by pulmonary tumor response in strain A mice. Cancer Res. 35:1411 - 1415.

Proctor, N.H., Hughes, J.P., 1978. Chemical hazards of the workplace. J.B. Lippincott Co., Philadelphia, Pa.

Roycroft, J., 1989. Toxicology and carcinogenesis studies of bromoethane in F344/N rats and B6C3F$_1$ mice. Public Health Service, U.S. Department of Health and Human Services. NIH Publication no. 90-2818.

Roycroft, J.; Ragan, H.; Miller, R.; Renne, R., Chou, B., 1989. Toxicologic and carcinogenic effects of two-year inhalation exposure to bromoethane or chloroethane in rats and mice. Proc. Am. Assoc. Cancer Res. 30.115 (Abstract).

Sax, N.I.; Lewis, R.J. Sr., 1988. Dangerous properties of industrial materials. 7th ed. Van Nostrand Reinhold Co., New York.

Tatkin, R.L.; Lewis, R.J. Sr., 1983. Registry of toxic effects of chemical substances. 1981 edition, Vol. 2, Public Health Service, U.S. Department of Health and Human Services.

Windholz, M., 1976. The Merck Index. 9th ed. Merck and Co., Inc., Rahway, N.J.

APPENDIX I: THEORETICAL ANALYSIS

THEORETICAL ANALYSIS

When the vapor of a compound is allowed to come to equilibrium with a solid surface, the concentration of the compound is always found to be greater on the surface than in the free gas. This process forms the basis of an equilibrium adsorption system for removing an adsorbable compound (a sorbate) using a porous solid adsorbent.

For a component of a mixture, at a fixed temperature, the adsorbed phase concentration of that component is a function of the partial pressure in the gas phase. Experimentally we can determine the adsorbed phase concentration as a function of partial pressure of that component - the resulting plot is the adsorption equilibrium isotherm. Isotherms show two distinct regions. At low concentrations, the amount adsorbed is directly proportional to the partial pressure:

$$q = Kp$$

where: q is the adsorbed phase concentration of a component

p is the partial pressure of the component in the gas phase

K is an equilibrium constant.

At high concentrations, there is a region where the amount adsorbed is not a strong function of the partial pressure. For very high partial pressures, the amount adsorbed reaches a maximum called the saturation limit. When adsorption occurs, the heat adsorbed is called the heat of adsorption. Knowing the equilibrium constant as a function of temperature, the heat of adsorption can be calculated using the following equation:

$$K = Ko \exp(-\Delta H/RT)$$

where: K is the equilibrium constant

T is the absolute temperature

Ko is the pre-exponential constant

R is the Universal Gas Constant (cal/gmol·°K)

ΔH is the heat of adsorption.

The strength of the sorbate/adsorbent interaction is quantified by the heat of adsorption. For large values, the energy required to remove the adsorbed compound is also large.

Adsorption equilibrium isotherms can be determined using gravimetric or volumetric methods. For sorbates that have high heats of adsorption and are adsorbed quickly, a constant temperature may be difficult to maintain using these methods, which may influence the equilibrium data. A chromatographic technique is a practical alternative to these more conventional techniques because intrusion of heat transfer resistances are essentially eliminated.

In a chromatographic experiment, an adsorption column is subjected to a perturbation in the sorbate concentration of the inlet stream and the response of the outlet concentration is monitored. This response plotted as a function of time is the breakthrough curve. The perturbation can either be a pulse or a step input in concentration - the same information can be obtained from either. In this study a step was used.

For a symmetrical breakthrough curve, the mean residence time t_B, is equal to the mid-point time, i.e.

$$t_B = t,\ C/C_o = 0.5$$

where: C is the outlet sorbate concentration at time t

Co is the initial concentration at the inlet.

For each breakthrough curve we can obtain the effective equilibrium constant, *K*, according to:

$$K = m\left[\frac{t_s}{L/V} - 1\right]$$

where: $m = \epsilon/(1 - \epsilon)$, the void volume per unit solid volume in the bed

L = length of the bed

V = interstitial velocity in the bed,

= $\frac{\text{volumetric flow}}{A \cdot \epsilon}$, A is cross sectional area of the bed

The effective equilibrium constant is the sum of the equilibrium constants for the helium gas carrier and the adsorbable component:

$$K = K_1x_1 + K_2x_2$$

where: K_1 is the helium equilibrium constant

K_2 is the sorbate equilibrium constant

x_1 is the mole fraction of helium

x_2 is the mole fraction of the sorbate.

The amount of carrier gas (in most cases, helium) adsorbed is generally considered to be negligible compared to the sorbate concentration, i.e. $K_1 >> K_2$. For binary systems, as $x_1 \rightarrow 0$ and $x_2 \rightarrow 1$ (helium is component 1), the above equation is true and for strongly adsorbed species as $x_1 \rightarrow 1$ and $x_2 \rightarrow 0$, the equation will also hold true.